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Effect of Humidity on Carbon Adsorption Performance in Removing Organics from Contaminated Air Streams

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16. ABSTRACT The paper describes the configuration of EPA's inhouse, automated, adsorption laboratory, operation of the laboratory, experimental design for evaluating single-component adsorption in the presence of humidity, and results to date. An objective of the laboratory is to characterize the effects of relative humidity (RH) on performance at the lowest concentrations of concern for potentially toxic organic pollutants. Tests have been performed to characterize the effect of humidity on the removal of volatile organics from contaminated air streams at concentrations ranging from 100 to 2000 ppmv. Three compounds, toluene, ethanol, and methyl ethyl ketone (MEK), were independently tested with a RH range between 30 and 70%. These tests were performed on activated carbon (BPL 4x10 mesh) on two bed columns, 15.2 cm in diameter and 15.2 cm deep.

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Pollution Organic Compounds Toxicity Adsorption Activated Carbon Humidity Toluene Ethanols Methyl Ethyl Ketone	Pollution Control Stationary Sources	13B 07C 06T 14G 11G 04B

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EFFECT OF HUMIDITY ON CARBON ADSORPTION PERFORMANCE IN REMOVING ORGANICS FROM CONTAMINATED AIR STREAMS

BY

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INTRODUCTION

Adsorption is a technique that has been widely used for many years in the separation of substances from either gaseous or liquid streams. It involves a selective separation of compounds from a fluid phase onto the surface of a solid substrate known as the adsorbent. Many adsorbents have been developed to achieve the separation of specific substances. Activated carbon is generally the adsorbent of choice. In the liquid phase, activated carbon has been widely used to remove solvents from contaminated groundwater, to clarify wastewater streams, and to remove colored impurities from refined sugar.

Activated carbon has been used in such gas cleaning applications as personnel protection (e.g., gas masks), air pollution control (e.g., solvent recovery from printing operations and emission controls on exhaust vents from coating and other industrial operations), and evaporative emission control in automobiles. Air pollution control applications are typically driven by economics and are generally applied to waste streams having high adsorbate concentrations (>500 ppmv).

Despite carbon adsorption's widespread and effective use for air pollution control, several areas remain where a better understanding of adsorbent technology could make an impact resulting in improved pollution control. Most carbon manufacturers are reluctant to divulge detailed design information. The available data pertain mostly to single component waste streams, at low humidity levels. Obtaining a better understanding of humidity effects should result in improved control efficiencies as would improved understanding of the multicomponent adsorption of both organic solvents and water. Finally, improvements of adsorber operation could impact control effectiveness. The development of improved adsorbents allowing almost perfect removal is also important. It was with an eye toward these areas that the EPA's Air and Energy Engineering Research Laboratory (AEERL) designed and constructed a semi-pilot scale adsorption facility.

The presence of water vapor in an emission stream can have a profound effect on the adsorption of organic vapors, both singly and in mixtures. However, this effect has not been quantified in the open literature and is not widely understood. Hence, initial effort in the laboratory has been focused on the effect of humidity on the adsorption of single organic compounds. Three humidity levels (H) were used in conjuction with two levels of temperature (T), and two levels of concentration (C) for three challenge chemicals. Data were developed which supported the primary objective of determining which measurement of water vapor content, whether relative or absolute humidity (dew

point), most directly relates to adsorption capacity. The most important humidity measure is defined as the one whose response is most independent of temperature. A detailed discussion of relative versus absolute humidity effects is presented in a companion paper prepared for this meeting.[1] The present manuscript will focus on the laboratory, on the data developed, and on the magnitude of the humidity-challenge concentration interaction.

EXPERIMENTAL

Chemicals and Sorbent

Three volatile organic compounds, toluene, ethanol, and methyl ethyl ketone (MEK), were fed into a preconditioned air stream as a single organic at nominal concentrations of 200 and 1000 ppmv.

The sorbent used for these experiments was activated carbon, Calgon BPL 4/10 mesh with the following physical characteristics:[2]

Total Surface Area (N_2, BET Method), m^2/g	1050 - 1150
Apparent Density (Bulk Density, Dense Packing), Typical, g/cm^3	0.48
Particle Density (Hg Displacement), g/cm^3	0.85
Real Density (He Displacement), g/cm^3	2.1
Pore Volume (Within Particle), cm^3/g	0.7
Voids in Dense Packed Column, %	43
Specific Heat at 100 °C (cal/g °C)	0.25

Experimental Design

For each of the three challenge chemicals, an experimental design of the form shown in Table I was used. This statistical design was developed to explore the humidity variable of greatest importance to adsorption modeling, while allowing an analysis of the general effect of humidity on adsorption capacity.[1] The symbols + and - refer to the high and low values of each independent variable (see Table II). The order of runs was randomized for each organic compound. The number of runs in this test phase was intentionally set at a minimum. As such, replication of runs was avoided. However,

several runs were added after completion of the 24-run test plan.

TABLE I. PHASE I TEST PLAN

Run Set No.	T	H	C
1	+	+	-
2	+	-	+
3	-	+	+
4	-	-	-
5	-	-	+
6	+	+	+

* Each run set corresponds to four runs.

TABLE II. SETTINGS OF INDEPENDENT VARIABLES FOR PHASE I TESTING

			-	+
Temperature, °C (°F)			29.4 (85)	48.9 (120)
Humidity (relative %)			30	70
Concentration (ppmv)			200	1000
Challenge Chemicals:	Toluene	(Aromatic)		
	Ethanol	(Alcohol)		
	MEK	(Ketone)		

Apparatus

A semi-pilot scale adsorption system, schematically shown in Fig. 1, was used for all the experiments. The system consists of two major components: the challenge, and the regeneration subsystems. The first subsystem provides a known challenge stream to the adsorbers and also includes the adsorption beds. The other includes the means of regenerating the saturated carbon beds. These two processes are controlled electronically using OPTO-22™ control unit interfacing with a data acquisition unit. This data acquisition unit stores data automatically while monitoring the process setpoint values used during the system operation. The analytical equipment consists of a

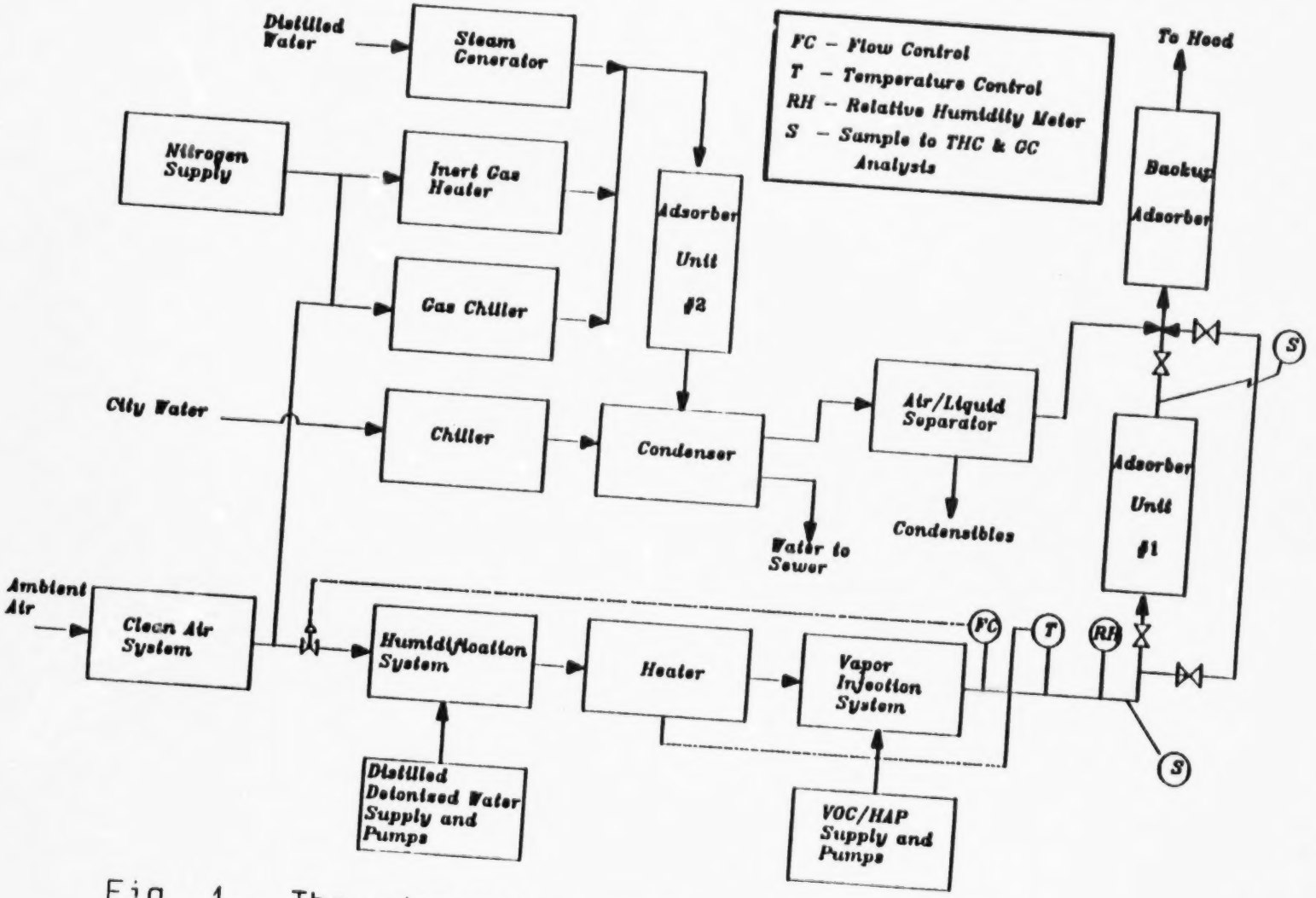


Fig. 1. The adsorption system.

gas chromatograph (GC) used as a total hydrocarbon (THC) analyzer. Supported by a chromatography data acquisition system, this analytical equipment provides chemical analysis of the challenge (feed) and exhaust streams.

Two adsorption vessels were designed to allow a 50.8 by 15.2 cm nominal diameter of adsorbent material. The adsorbent beds are supported on stainless steel screens, and the columns are made with Schedule 10, Type 316 stainless steel pipe. Valving is provided to bypass both vessels or to challenge one while simultaneously regenerating the other. Inlet temperature, pressure, and differential pressure readings are taken at each vessel. Flow is distributed evenly by directing the gas stream through a bed of glass beads of similar size to the adsorbent before passing into the adsorbent bed. The direction of challenge flow is upward in order to avoid the accumulation of condensed steam in the beds during countercurrent regeneration.

Ambient air is passed through a clean air unit (Zern Industries) that removes particles, moisture, and non-methane hydrocarbons. This air stream is heated by a Hotwatt Inc. electric heater. The temperature control sensing element is located downstream just after the flow sensor and prior to the adsorbers. This allows the heater to be modulated to provide additional heat for pipe losses as well as heat of vaporization for the injected volatile organic compounds (VOCs).

At the outlet of the air heater, the humidifier delivers the required moisture for air stream humidification. The humidifier is constructed from a Watlow 6 kW electric circulation heater. The heater is controlled at 232 to 288 °C. Water is delivered to the heater from a polycarbonate reservoir by a Perkin Elmer high performance liquid chromatography (HPLC) pump. This pump delivers a constant measured flow of water which is evaporated and combined with the challenge stream. A 121.9 cm mixing section blends the heated air and vapor from the humidifier. The moisture content is then monitored at the outlet of the mixing section by a dew point hygrometer from General Eastern. Moisture content is also checked by a water material balance at the end of each test.

Flow control on the air stream is provided by the use of a control valve located in the dry air line. This valve will be controlled electronically based on information provided by mass flow measurement at the adsorber inlet. A bypass mode of operation is used to established stable challenge stream operating conditions such as temperature, humidity, and flowrate. Once operating conditions are stabilized the run is initiated. A backup adsorber filled with 136 kg of activated carbon is used to prevent release of test organics into the atmosphere.

A single VOC is fed into the challenge stream by a second Perkin Elmer HPLC pump at a specific rate by manual adjustment. The inlet challenge stream is sampled at a point common to both vessels while the outlets are individually sampled. The concentration for both inlet and outlet streams is monitored by a Shimadzu 2A gas chromatograph with a flame ionization detector operating as a total hydrocarbon analyzer. An IBM-PC and a data acquisition program (Labtech Notebook) are used to acquire data and display in real time both the inlet and outlet concentrations.

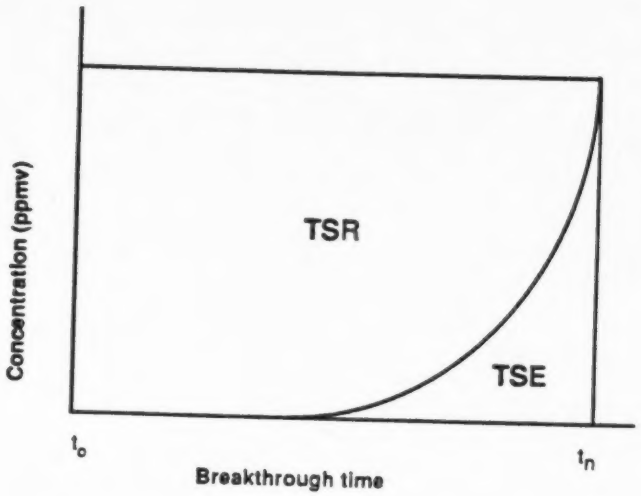
There are three regeneration modes available: steam stripping, nitrogen purge, and air purge. All three modes are available during any regeneration cycle. Steam for stripping is provided by an Electro Steam steam generator.

Procedure

The experiments were carried out at 34 Nm^3/h, 29.4 and 48.9 ^oC, and relative humidities (RHs) ranging from 0 to 90 %. About 1.4 kg of activated carbon were packed in each column. Since several preliminary tests were carried out before phase I, a working capacity was established. This working capacity was defined by the regenerating conditions used during all the laboratory operations. Single injection of toluene, ethanol, and MEK was conducted individually at concentrations of 200 and 1000 ppmv. The experimental procedure consisted of measuring the time of 50 % breakthrough (when the outlet concentration reaches 50 % of the inlet concentration). Since the breakthrough curve was assumed to be symmetrical, the 50 % breakthrough will provide a good estimate of the working capacity of the sorbent for a particular adsorbate. The flowrate to which the adsorbers were subjected neglects mass transfer effects.

Regeneration was achieved by low temperature ($\approx$ 110 ^oC) and low pressure ($\approx$ 137 kPa) steam at a rate of 2 kg of steam per kg of carbon. Steaming was followed by hot and cold air to dry the beds and restore operating conditions. Water and adsorbate vapors were condensed and collected during regeneration, then the organic was separated from the aqueous phase by gravimetric decantation.

To account for solvent mass balance, the total solvent injected (TSI) was recorded along with the total solvent retained (TSR) in the adsorbent before regeneration. These values were then compared with values obtained from the breakthrough curve to obtain percent of solvent recovered (see Fig. 2).



TSR ≡ Total Solvent Retained TSE ≡ Total Solvent Emitted

Fig. 2. Breakthrough curve to estimate solvent material balance.

The percent of total solvent recovered after certain percent breakthrough was expressed as:

$$\text{Total Solvent Recovered} = \frac{\text{TSR} + \text{TSE}}{\text{TSI}} \quad (100)$$

The value for the total solvent emitted (TSE) was estimated by calculating the area under the curve.

Toluene, being virtually insoluble in water, was collected in the upper layer in the decanter, and then decanted for reuse. Ethanol and MEK were not separated by decantation because they are miscible in water. Their material balances were estimated comparing the water collected during toluene tests and the total solvent collected during ethanol and MEK, respectively. In addition to the organic mass balance, a water mass balance was also done. During adsorber regeneration, vapors were condensed and (when possible) water and organic solvent were separated. The weights were recorded and compared to the expected amount of water to be used during the regeneration cycle.

A set of standard runs was implemented to characterize any significant short term

reduction in the sorbent capacity. The standard runs consisted of four runs of toluene at 1000 ppmv, 29.4 °C, and 50 % relative humidity. These tests were made after the set of runs for each organic compound.

RESULTS AND DISCUSSION

Figs. 3a and 3b show the adsorption capacity for toluene, ethanol, and MEK at two different concentrations and 30 % relative humidity. At these conditions ethanol appears to be more sensitive to changes in concentration than toluene or MEK in the concentration range considered. Toluene and MEK, being less sensitive to changes in concentration, are preferentially adsorbed by activated carbon. This is an indication of the steepness of ethanol's isotherm as compared to toluene and even MEK.

Since the surface of activated carbons is usually nonpolar, compounds with high London forces would be more preferentially adsorbed than polar compounds. However, some polarity may arise on the adsorbent from surface oxidation created during carbon production or as carbon is regenerated with steam.[3,4] This surface oxidation may enhance the adsorption of polar compounds including water.

When more than one compound is fed to an adsorbent, competition between components for active sites will be established.[5] Partial pressure, molecular form and size, and polarity are some of the factors which may help components to be successful in their "fight for sites."[6] For one of the binary mixtures used in these experiments, water vapor and toluene, toluene has to absorb or displace the water already adsorbed in the active sites. This displacement would be easier if the partial pressure of water vapor were not as high compared to toluene's partial pressure. In addition at high concentrations of water vapor, condensation may occur creating more difficulty for its displacement. On the other hand, if a polar organic such as ethanol is fed instead of toluene, its adsorption may be enhanced or not affected if water is present in the sorbent surface (see Fig. 7a). The presence of water may help the polar organic to access the active sites.

Figure 4 shows the dramatic effect that high humidity has on the performance of activated carbon adsorption. This figure presents data for toluene adsorption at 1000 ppmv and varying humidity. At high RH values most of the pores are filled with water and the sorbent capacity is substantially reduced. A similar effect is seen in Figs. 5a and 5b, where toluene adsorption at two temperatures is shown. In Fig. 5b, the temperature is increased while keeping the same respective values of relative humidity. An even more significant decrease in adsorption capacity is observed at the higher temperature.

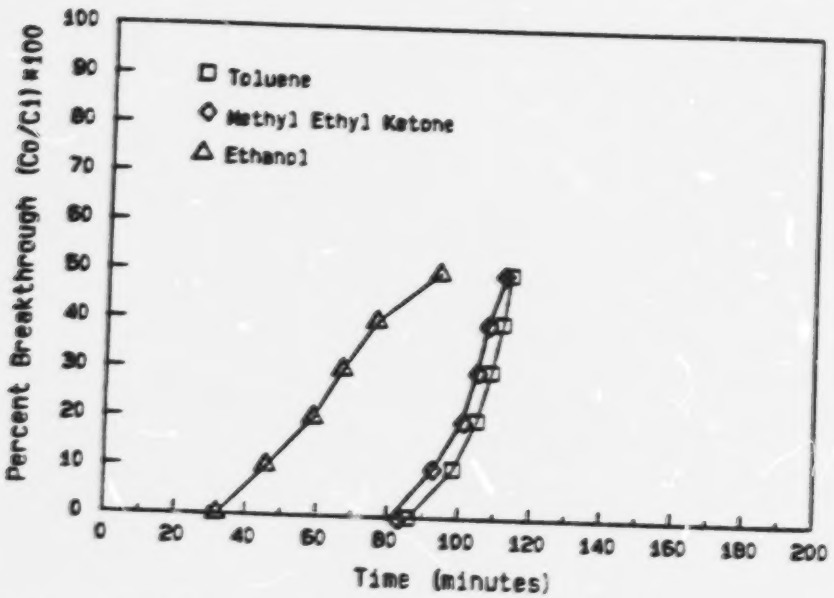


Fig. 3a. Comparison of breakthrough time of toluene, ethanol, and MEK at 29.4 °C, 30% RH, and 1000 ppmv.

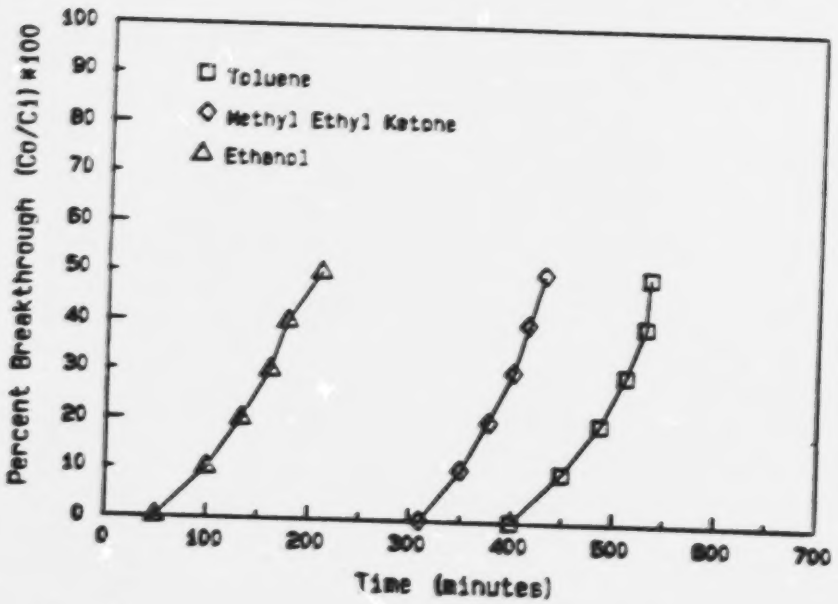


Fig. 3b. Comparison of breakthrough time of toluene, ethanol, and MEK at 29.4 °C, 30% RH, and 200 ppmv.

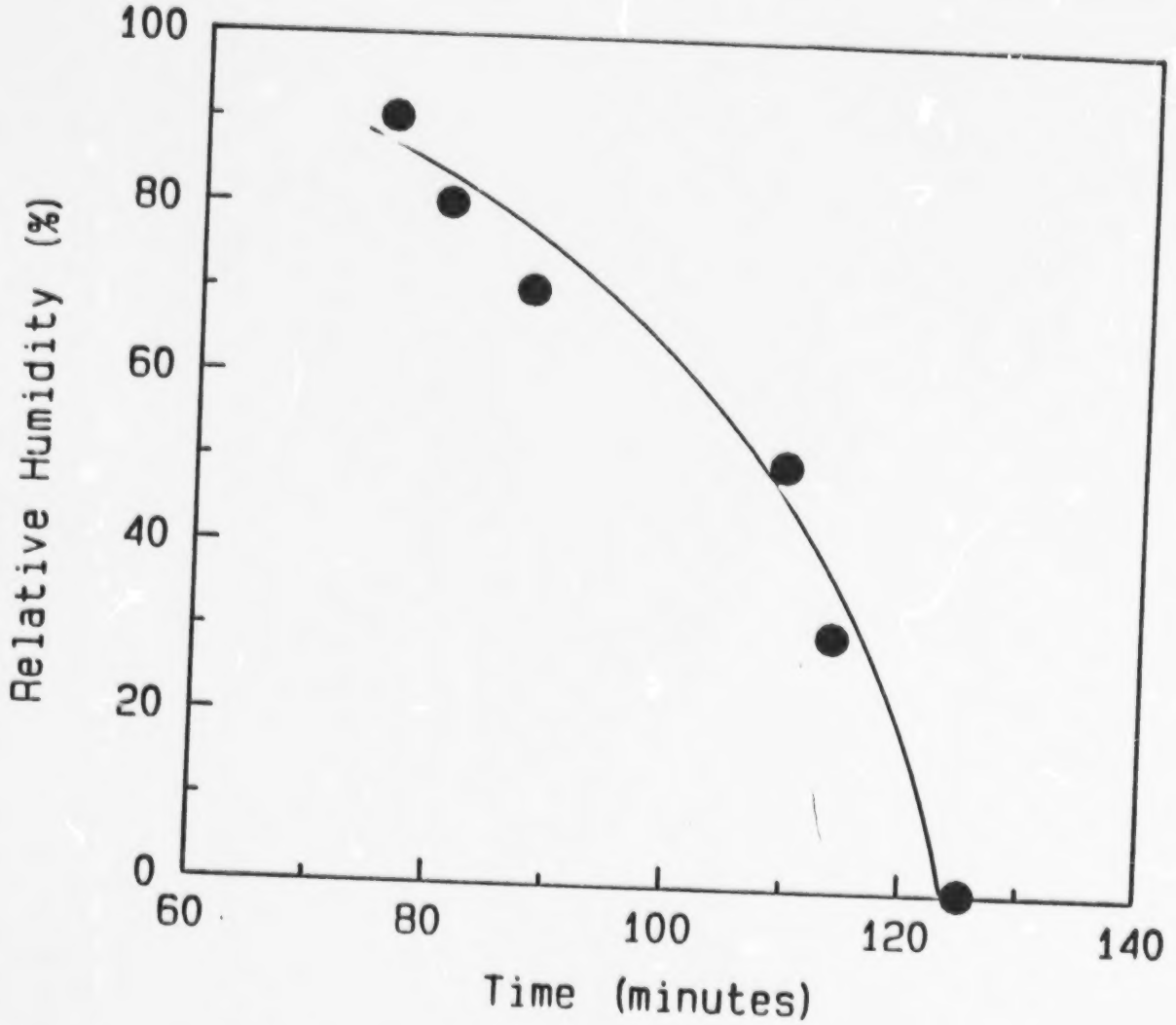


Fig. 4. Effect of relative humidity on time to 50% breakthrough for 1000 ppmv toluene.

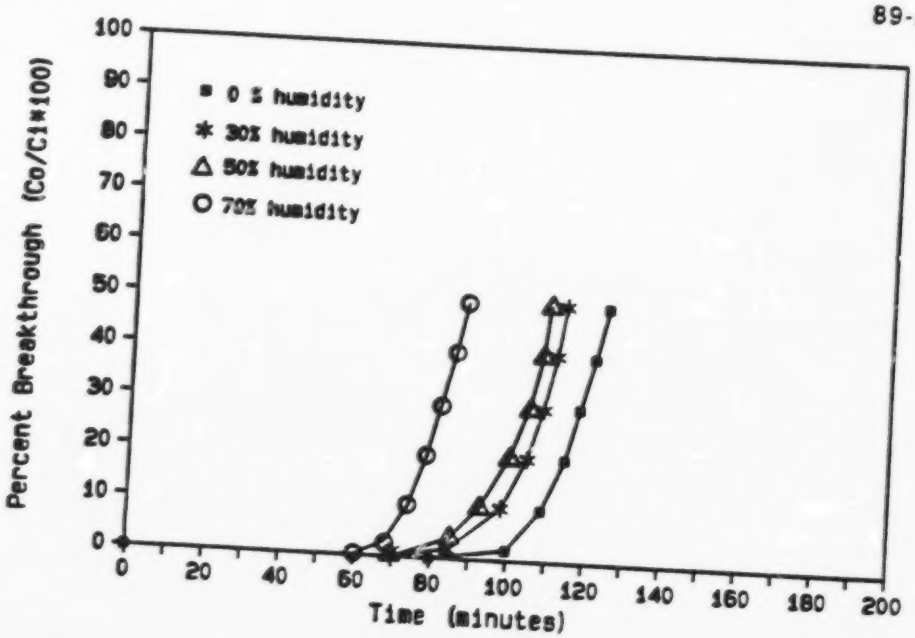


Fig. 5a. Comparison of breakthrough time for toluene at 1000 ppmv and 29.4 °C for various humidities.

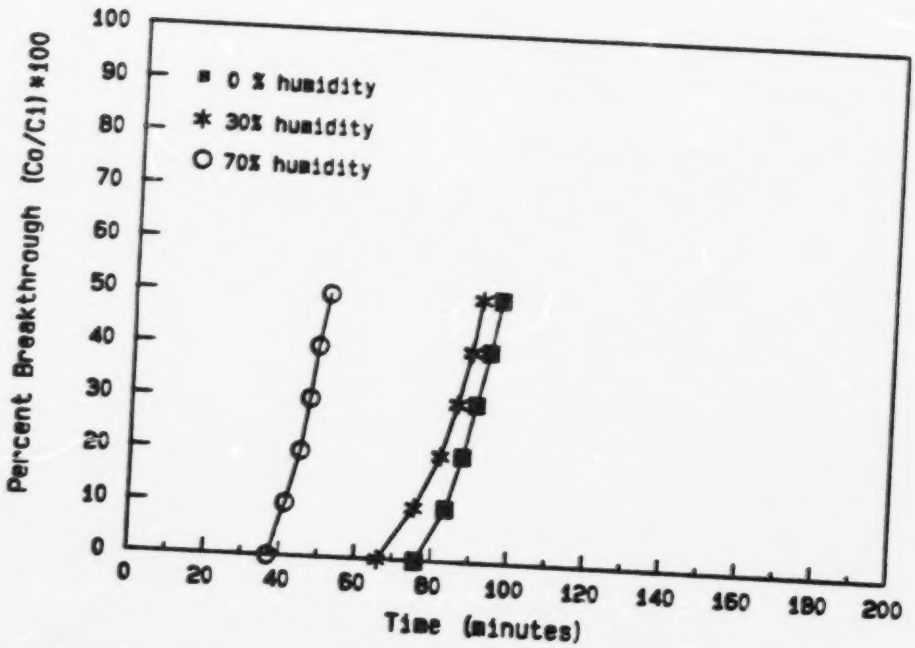


Fig. 5a. Comparison of breakthrough time for toluene at 1000 ppmv and 48.9 °C for various humidities.

The temperature effect on adsorption capacity is particularly shown at no moisture. Figs. 6a, 6b, 7a, and 7b show the result for MEK and ethanol, respectively. At the lower temperature and moisture content, MEK behaves similarly to toluene. However, when these two parameters are raised the effect in capacity is more dramatically noticed in MEK. In Fig. 7a the adsorption for ethanol seems to improve at 30% RH, although more data are necessary to verify this behavior.

Tables IIIa, IIIb, and IV show the decrease in adsorbent capacity due to a combined effect of temperature and relative humidity. Since the influent concentration and flowrate were constant within each table, the adsorbent capacity is reflected by time to 50% breakthrough. In Tables IIIa and IIIb the reduction in capacity was obtained by comparing the capacity at 29.4 °C with the one at 48.9 °C at the RHs and solvent concentrations indicated in the tables. In Table IV the effect of RH on carbon performance was obtained by comparing capacity at several RHs, keeping temperature constant. At 200 ppmv the decrease in capacity obtained for toluene and MEK was about 70 % comparing capacities at 30 and 70% RH. This indicates that carbon performance is affected by RH, especially when the adsorbate is at low concentration.[7]

During these experiments there was no evidence of a significant decrease in adsorption capacity. In fact, after the set of runs for ethanol were completed, the first two runs of the standard test showed a temporary increase (≈ 25%) of the sorbent capacity. When the last two runs of the standard test were completed, the sorbent capacity returned to the working capacity obtained during previous standard runs.

CONCLUSIONS

Based on the work to date the following conclusions can be drawn:

1. Activated carbon adsorbs toluene or MEK better than ethanol at the concentration levels used in these experiments.
2. Activated carbon performance is affected by the level of relative humidity and the temperature at which the sorbent is exposed. This effect is more dramatically seen at the low level of concentration examined.
3. No significant degradation leading to reduction of the sorbent capacity was observed. On the other hand, a temporary increase of the working capacity was seen after the sorbents were challenged with ethanol.
4. The effect of relative humidity on carbon adsorption performance is difficult to characterize at low concentrations given the amount of data available.

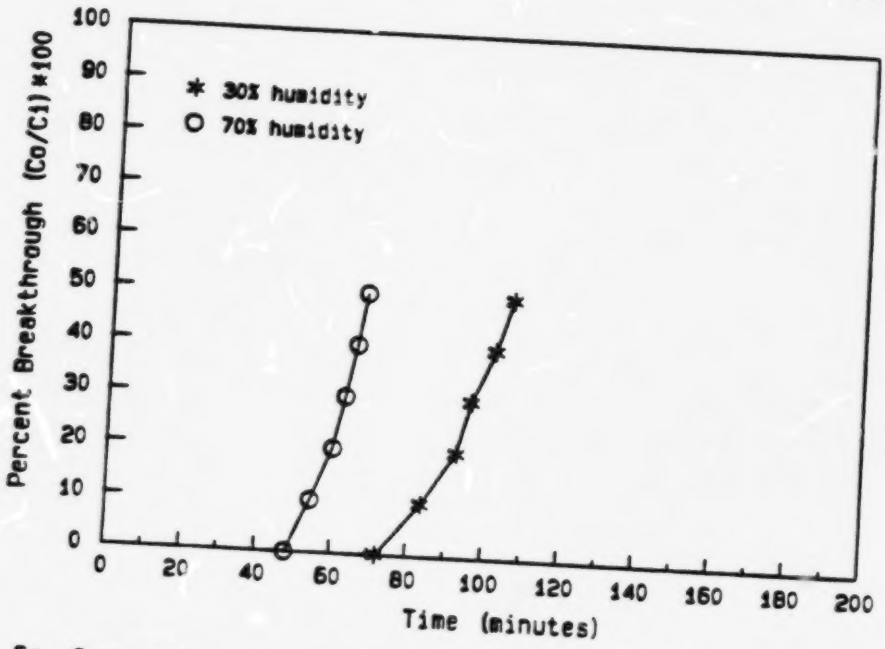


Fig. 6a. Comparison of breakthrough for MEK at 1000 ppmv and 29.4 °C for various humidities.

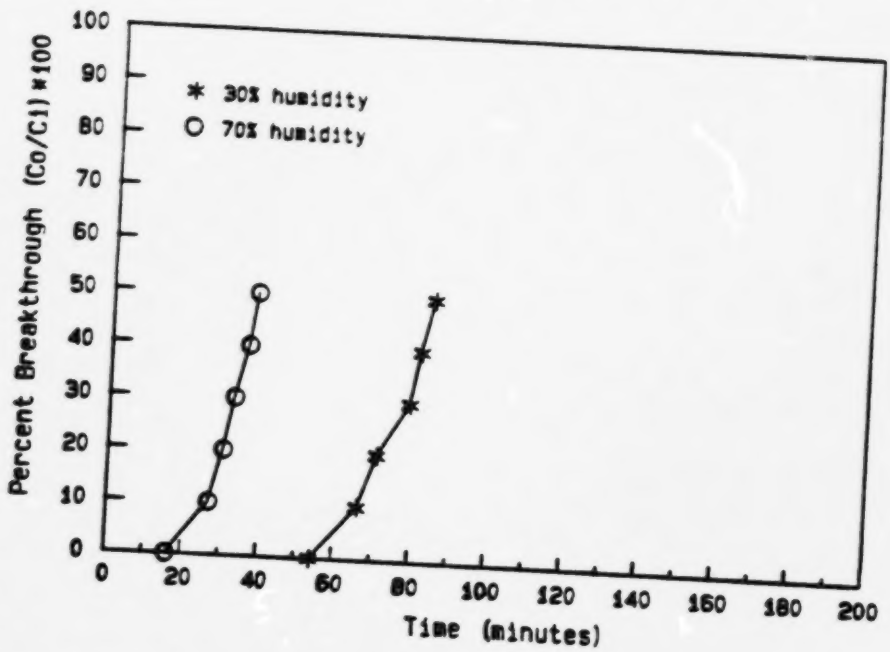


Fig. 6b. Comparison of breakthrough for MEK at 1000 ppmv and 48.9 °C for various humidities.

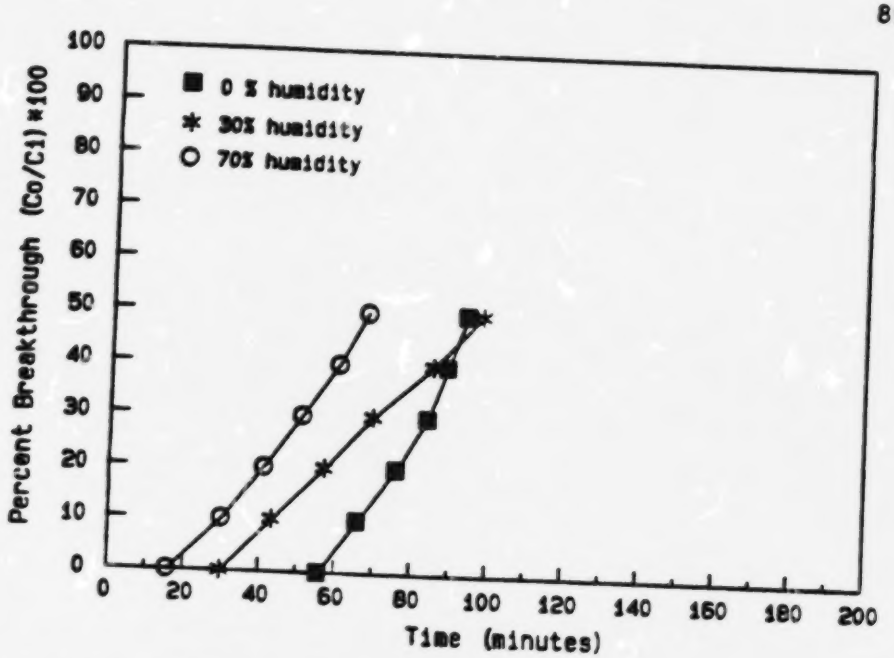


Fig. 7a. Comparison of breakthrough time for ethanol at 1000 ppmv and 29.4 °C for various humidities.

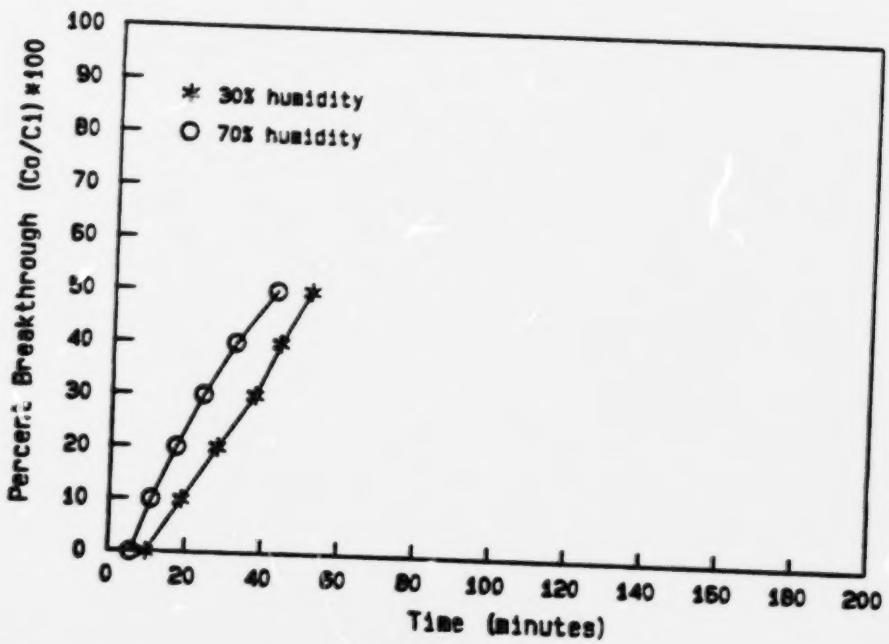


Fig. 7b. Comparison of breakthrough time for ethanol at 1000 ppmv and 48.9 °C for various humidities.

TABLE IIIa. COMBINED EFFECT OF TEMPERATURE AND RELATIVE HUMIDITY ON SORBENT CAPACITY AT 1000 PPMV

Compound	Relative Humidity (%)	Time (minutes) at 29.4 °C	Time (minutes) at 48.9 °C	Capacity Reduction (%)
Toluene	0	125	96	23
	30	114	91	20
	70	88	57	35
Ethanol	30	98	52	47
	70	68	43	37
MEK	30	106	85	20
	70	67	38	43

TABLE IIIb. COMBINED EFFECT OF TEMPERATURE AND RELATIVE HUMIDITY ON SORBENT CAPACITY AT 200 PPMV

Compound	Relative Humidity (%)	Time (minutes) at 29.4 °C	Time (minutes) at 48.9 °C	Capacity Reduction (%)
Toluene	0	---	---	---
	30	---	---	---
	70	155	67	57
Ethanol	30	---	---	---
	70	---	---	---
MEK	30	---	---	---
	70	129	33	74

TABLE IV. THE EFFECT OF RELATIVE HUMIDITY ON SORBENT CAPACITY (AT 1000 PPMV)

Compound	RH1	RH2	Temp. = 29.4°C			Temp. = 48.9°C		
			Time (minutes) at RH1	Time (minutes) at RH2	Capacity Reduction (%)	Time (minutes) at RH1	Time (minutes) at RH2	Capacity Reduction (%)
Toluene	0	30	125	114	9	96	91	5
	0	50	125	109	13	---	---	---
	0	70	125	88	30	96	57	41
	30	50	114	109	4	---	---	---
	30	70	114	88	23	91	57	38
Ethanol	0	30	94	98	(4)	---	---	---
	0	70	94	68	28	---	---	---
	30	70	98	68	31	52	43	17
MEK	30	70	106	67	37	85	38	55

Note: The () means increase in capacity.

NOMENCLATURE

			Units
TSE	≡	Total Solvent Emitted	ppmv · min
TSI	≡	Total Solvent Injected	ppmv · min
TSR	≡	Total Solvent Retained	ppmv · min
t_o	≡	initial time of test	minutes
t_n	≡	any time of breakthrough	minutes

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